

## LA-UR-21-25468

Approved for public release; distribution is unlimited.

Title: XCP- Computational Summer Workshop: Equation of State Overview

Author(s): Sheppard, Daniel Glen

Intended for: Seminar for the XCP summer school 2021

Issued: 2021-06-10

---

**Disclaimer:**

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by Triad National Security, LLC for the National Nuclear Security Administration of U.S. Department of Energy under contract 89233218CNA000001. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.



# **XCP-Computational Summer Workshop: Equation of State Overview**

Daniel Sheppard, XCP-5

June 9th, 2021

# Overview of the Equation of State Program

1. An overview of Equation of State (EOS) theory, some relevant physics, experiments, computational methods, and the SESAME database will be presented. The goal will be to describe what types of data and modeling are required to make an EOS that typically spans up to  $\sim 10^9$  GPa in pressure and  $10^9$  K in temperature.

# What is an EOS?

- EOS: A **constitutive relation** describing the interrelationship between different **thermodynamic variables** for a material.
- **Constitutive relation**: establish an organized relationship (not really a law of nature, like conservation of energy or momentum).
  - Analytical Equations of State
    - $PV = nRT$  (ideal gas)
    - $(P + (P + a \frac{n^2}{V^2})(V-nb) = nRT$  (Vander-Waals equation)
    - $P - P_0 = \gamma \rho (U - U_0)$  (Mie-Gruneisen equation of state)
  - Tabular EOS
    - SESAME (LANL)
    - LEOS (LLNL)
  - Graphics / Plots
    - What one sees in old literature.

# What is an EOS?

- Thermodynamic variables:

$T$  – temperature    $P$  – pressure

$G$  – Gibb's free energy    $H$  – enthalpy

$\rho$  – density    $U$  (or  $E$ ) – specific internal energy

$A$  (or  $F$ ) – Helmholtz's free energy    $S$  – entropy

$B_T$  – isothermal bulk modulus    $B_S$  – adiabatic bulk modulus

$C_V$  – constant volume heat capacity    $C_P$  – constant pressure heat capacity

$\alpha_P$  – thermal expansion at constant pressure    $\Gamma$  – Gruneisen parameter

# What is an EOS?

- General Thermodynamic Relations:
  - $G = H - TS$  (Gibb's-free energy equation)
  - $A = U - TS$  (Helmholtz's-free energy)
  - $H = U + PV$  (Enthalpy)
- Note on nomenclature
  - A and F are used interchangeably for Helmholtz-free energy
  - U and E are used interchangeably for internal energy

# What is an EOS?: Thermodynamic Relations

$$F = E - TS$$

$$dF = dE - TdS - SdT$$

$$= -SdT - PdV$$

$$dF = \left( \frac{\partial F}{\partial T} \right)_V dT + \left( \frac{\partial F}{\partial V} \right)_T dV$$

$$S = - \left( \frac{\partial F}{\partial T} \right)_V \longleftarrow \text{Entropy}$$

$$P = \rho^2 \left( \frac{\partial F}{\partial \rho} \right)_T \longleftarrow \text{Pressure}$$

$$E = F + TS = F - T \left( \frac{\partial F}{\partial T} \right)_V \longleftarrow \text{Internal energy}$$

# What is an EOS?: Thermodynamic Relations

$$C_P = \left( \frac{\partial H}{\partial T} \right)_P = T \left( \frac{\partial S}{\partial T} \right)_P \quad \leftarrow \text{Specific heat at constant pressure}$$

$$B_T = V \left( \frac{\partial^2 F}{\partial V^2} \right)_T = -V \left( \frac{\partial P}{\partial V} \right)_T \quad \leftarrow \text{Isothermal bulk modulus}$$

$$B_S = -V \left( \frac{\partial P}{\partial V} \right)_S \quad \leftarrow \text{Adiabatic bulk modulus}$$

$$\frac{B_S}{B_T} = \frac{C_P}{C_V}$$

$$\gamma = \frac{\alpha B_s V}{C_p}$$

# What makes EOS useful?

- Materials manufacturing (metallurgy, annealing processes)
- Design of thermodynamic processes
- Power Production (car engines, jets engines, fuel cells)
- Air conditioning, refrigeration
- Distillations (oil and gas separations, whiskey)
- Supernova
- Core of the Earth
- Superconductivity

## Why do they matter? The Hydrodynamicist's View

Necessary to close the system of PDEs.

Suppose we want to know the state of a material as a function position and time.

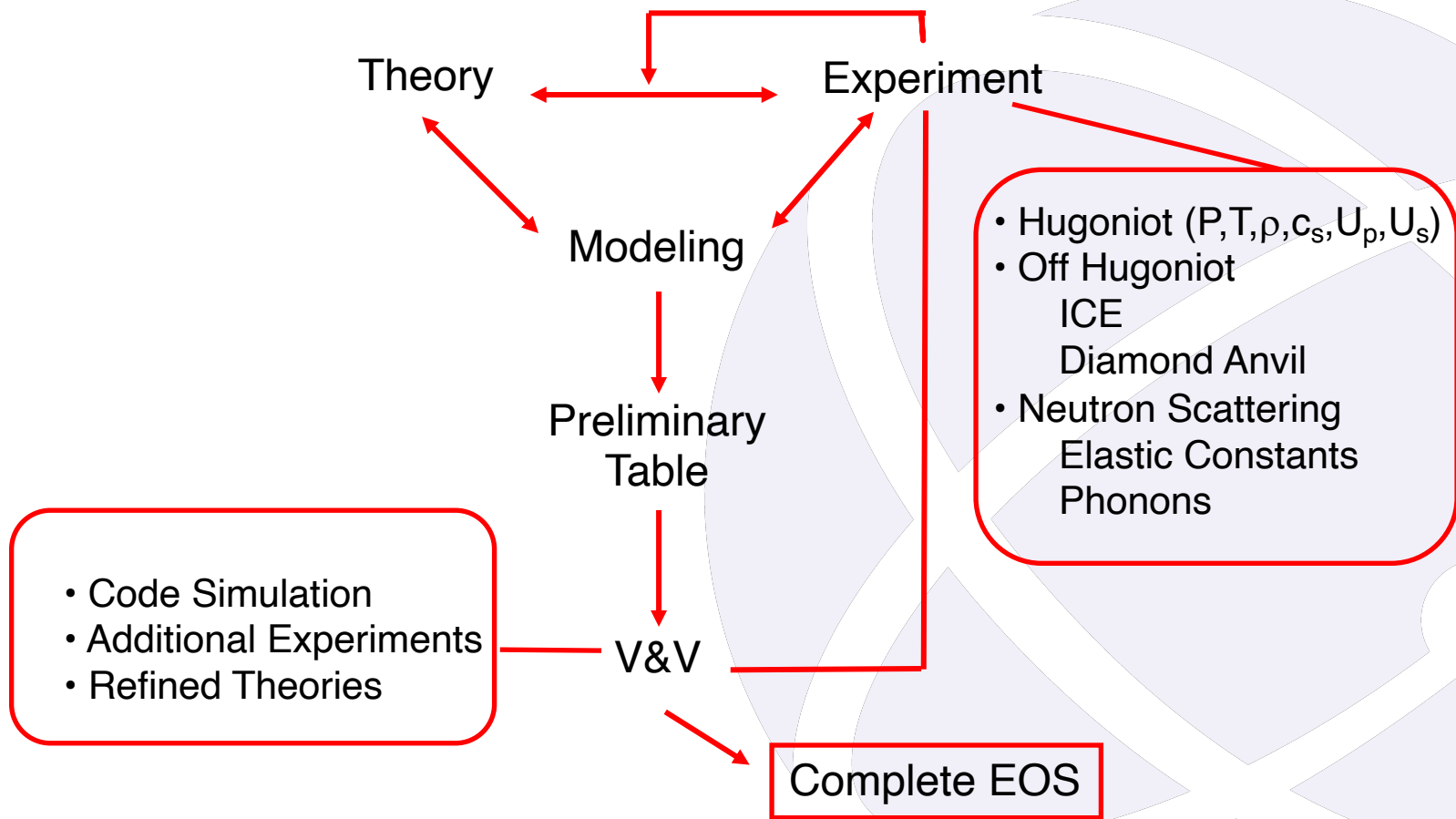
<u>Principle</u>	<u>Equation</u>	<u>Unknowns</u>	<u>No. Eqns.</u>
Mass	$\frac{\partial \rho}{\partial t} + \nabla \cdot \rho \mathbf{u} = 0$	4 ( $\rho, \mathbf{u}$ )	1
Newton's 2 <sup>nd</sup> Law	$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla P$	5 (+ $P$ )	4
Energy	$\rho \frac{\partial (u^2 / 2 + E)}{\partial t} + \rho \mathbf{u} \cdot \nabla (u^2 / 2 + E) = -\nabla \cdot P \mathbf{u}$	6 (+ $E$ )	5
<b>EOS</b>	$P = f(\rho, E)$	6 !	6

LA-UR-2024588

# The SESAME EOS library

- Developed @ LANL circa early 70's (before even I was born)
- Hundreds of tabular EOSs for a huge verity of materials ( eg. Metals, compounds, gases like air, H<sub>2</sub>).
- Tabulates  $P(\rho, T)$ ,  $U(\rho, T)$ ,  $A(\rho, T)$  other properties from thermodynamic manipulations
- Typical ranges of tables are: density  $10^{-6}$  g/cc –  $10^5$  g/cc , T 0 - $10^{12}$  K
- Each EOS is identified and accessed via a material integer ( 3719 and 3720 are Al EOSs)
- Used by LANL computational-physics codes (FLAG, xRage, Pagosa)
- Distributed to various other labs and universities around the globe

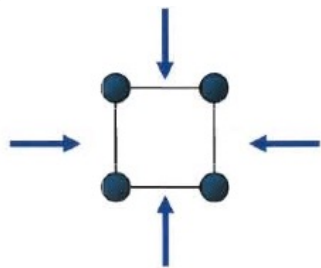
# Standard Approach to Making an EOS



# Standard Sesame Equation of State

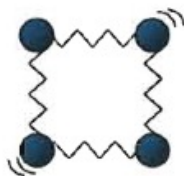
Three term Decomposition of the Free Energy

$$F(V, T) = \phi_0(V) + F_{\text{ion}}(V, T) + F_{\text{el}}(V, T)$$



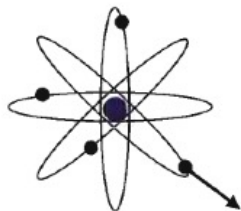
$\phi_0(V)$

cold curve contribution (LJ model,  
Mie-Gruneisen, TFD)



$F_{\text{ion}}(V, T)$

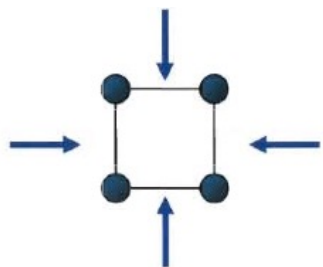
cold + thermal ionic contribution  
(Debye model with a correction for liquid)



$F_{\text{el}}(V, T)$

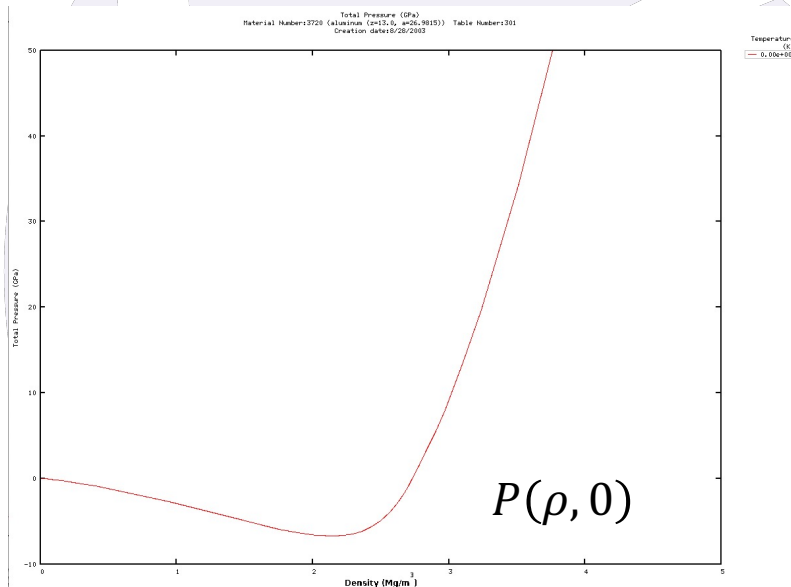
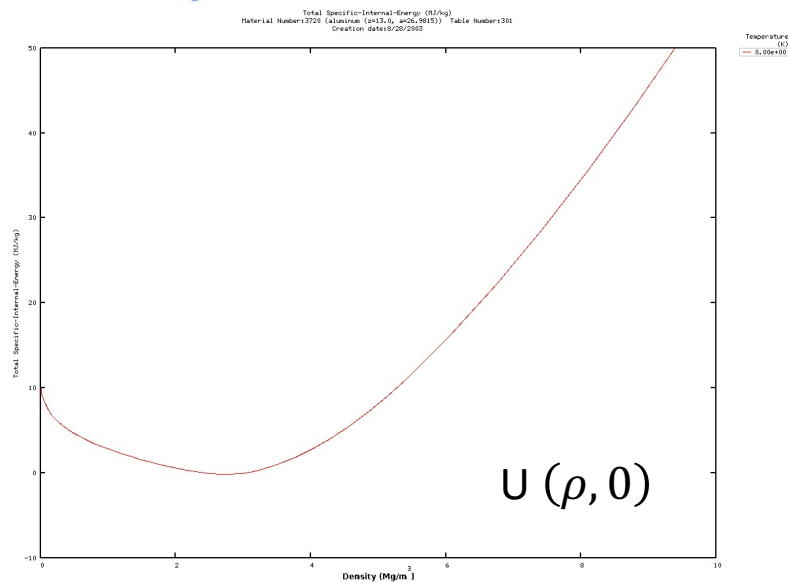
thermal electronic contribution  
(average atom TFD or Purgatory)

# Cold Curve: Compression response at T=0



$$\phi_0(V)$$

cold curve contribution (LJ model,  
Mie-Gruneisen, TFD)



# Standard Sesame Equation of State

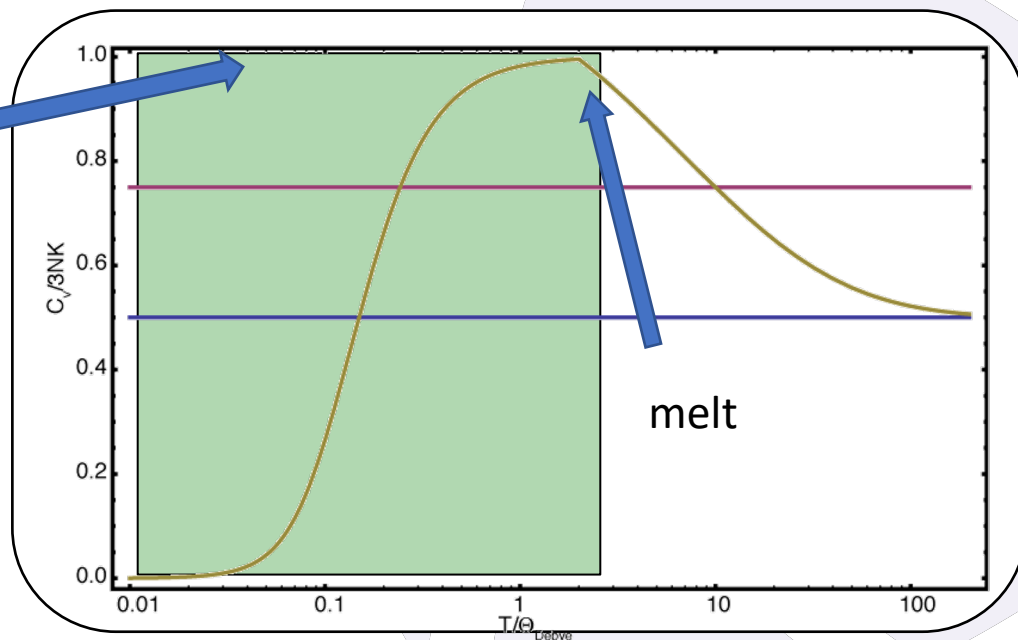


$$F_{\text{ion}}(V, T)$$

cold + thermal ionic contribution  
(Debye model with a correction for liquid)

Dulong-Petit limit

$$C_V = \frac{\partial U}{\partial T_V}$$



Solid Region

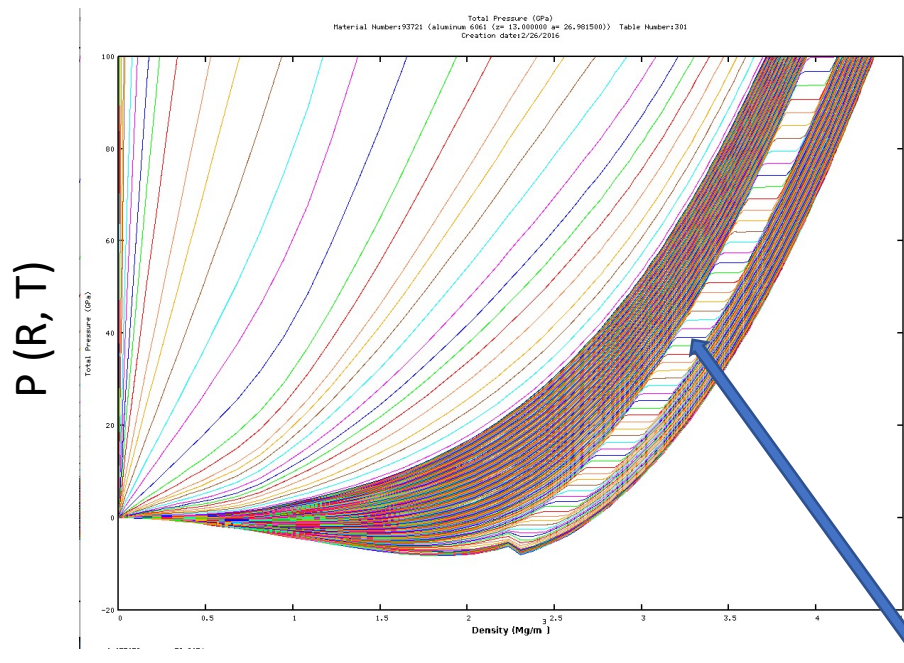
Liquid Region

# Standard Sesame Equation of State

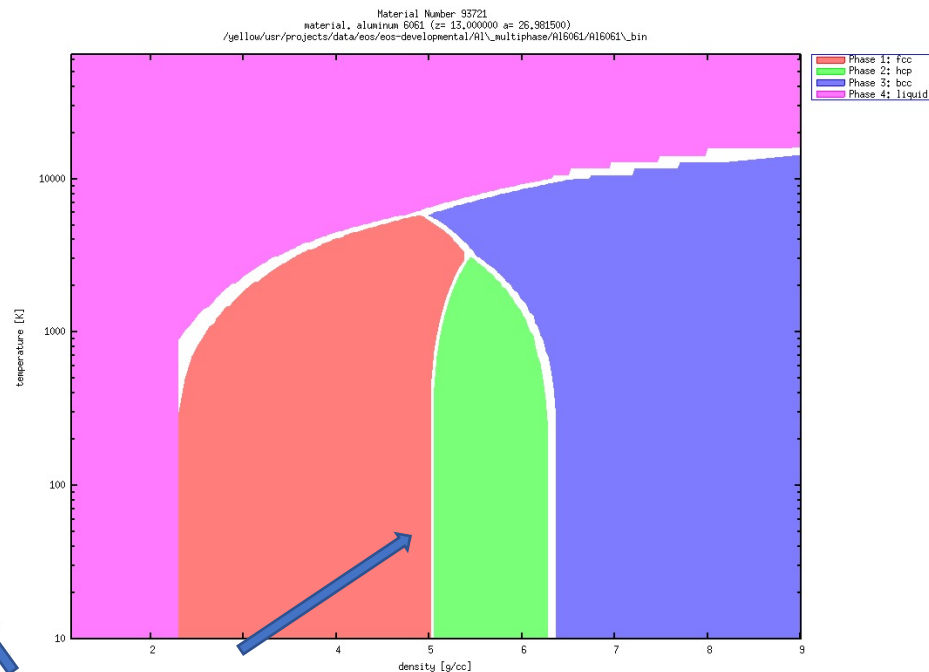
Al: Sesame 93721

Three term Decomposition of the Free Energy

$$F(V, T) = \phi_0(V) + F_{\text{ion}}(V, T) + F_{\text{el}}(V, T)$$

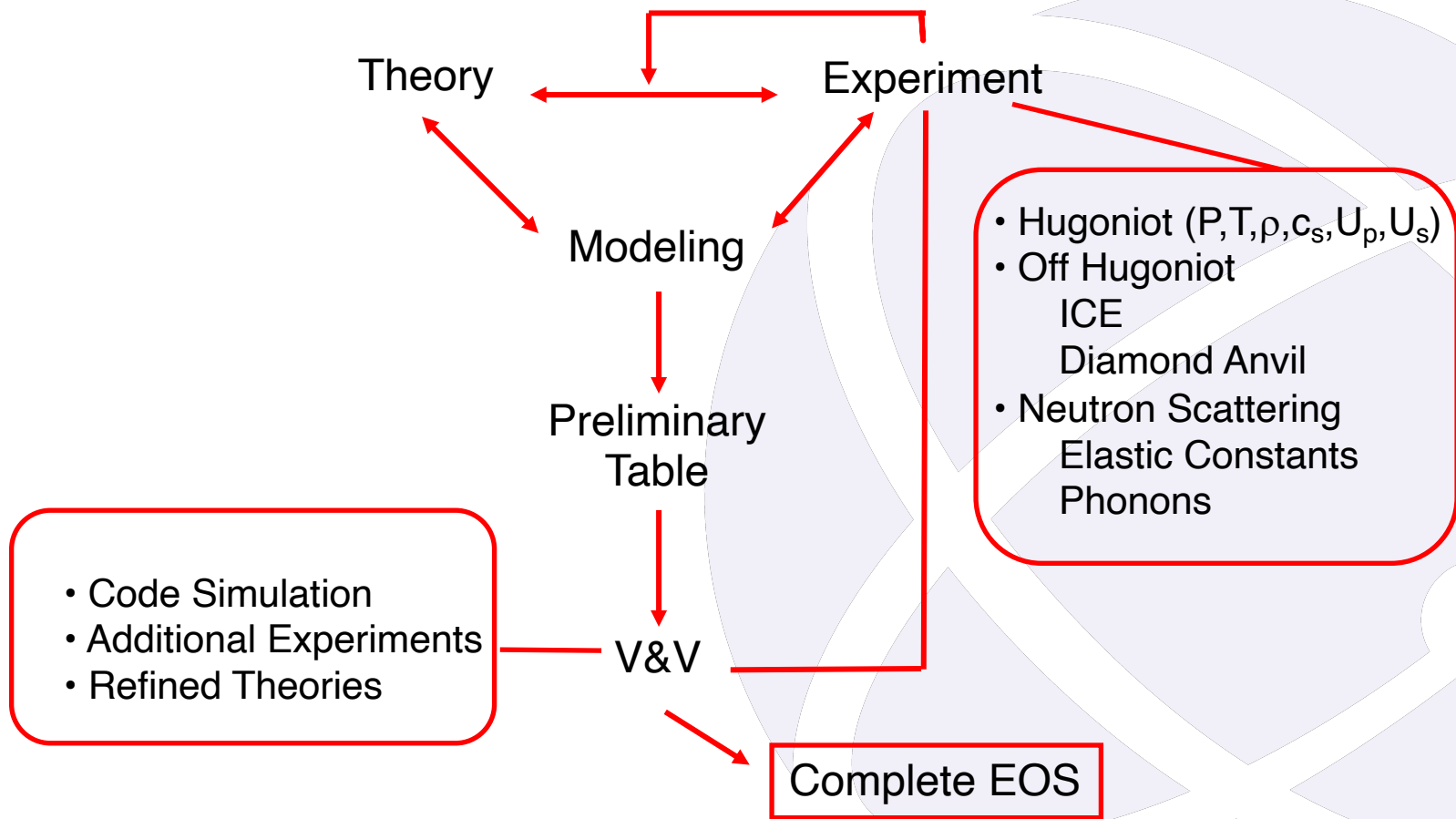


Iso-therms



Phase change

# Standard Approach to Making an EOS



# Experimentally Measured Data

- **Near-ambient Pressure Data**

- Density
- Melt and Boiling Point
- Thermal Expansion
- Acoustic Data
- Specific Heat
- Phonon / Elastic Moduli
- Isobaric

# Experimentally Measured Data

## • Near-ambient Pressure Data

- Density
- Melt and Boiling Point
- Thermal Expansion
- Acoustic Data
- Specific Heat
- Phonon / Elastic Moduli
- Isobaric

## • High Pressure Data

- Melt Curve
- Shock (Dynamic High Pressure)
- Diamond Anvil (Static High Pressure)
- Phonon/Elastic Moduli

## • Other Data

- Vapor curve
- Critical Point

# Shock Physics

The initial and final states are linked through the conservation of mass, momentum, and energy:

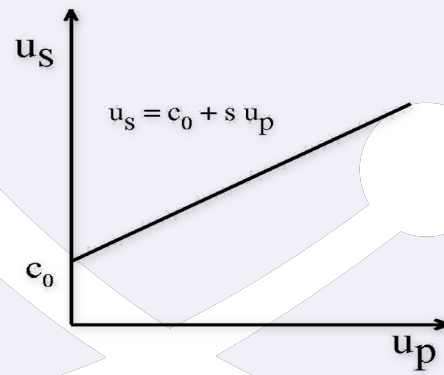
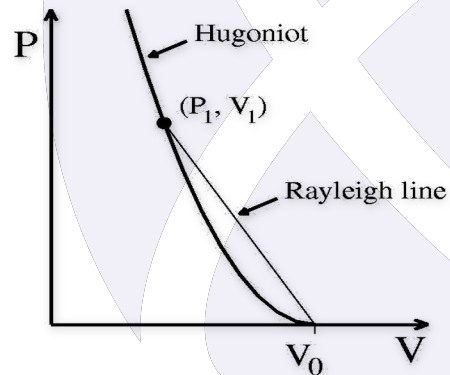
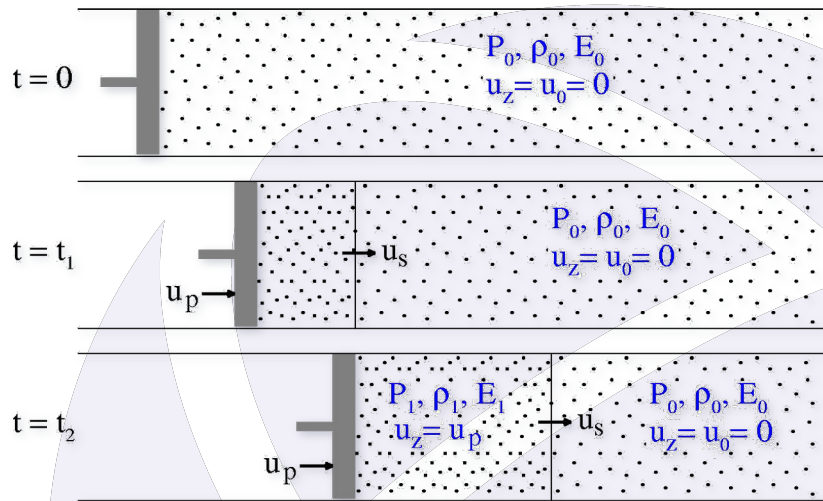
$$\varepsilon = 1 - \frac{\rho_0}{\rho_1} = 1 - \frac{V_1}{V_0} = \frac{u_p}{u_s}$$

$$P_1 = P_0 + \rho_0 u_s u_p$$

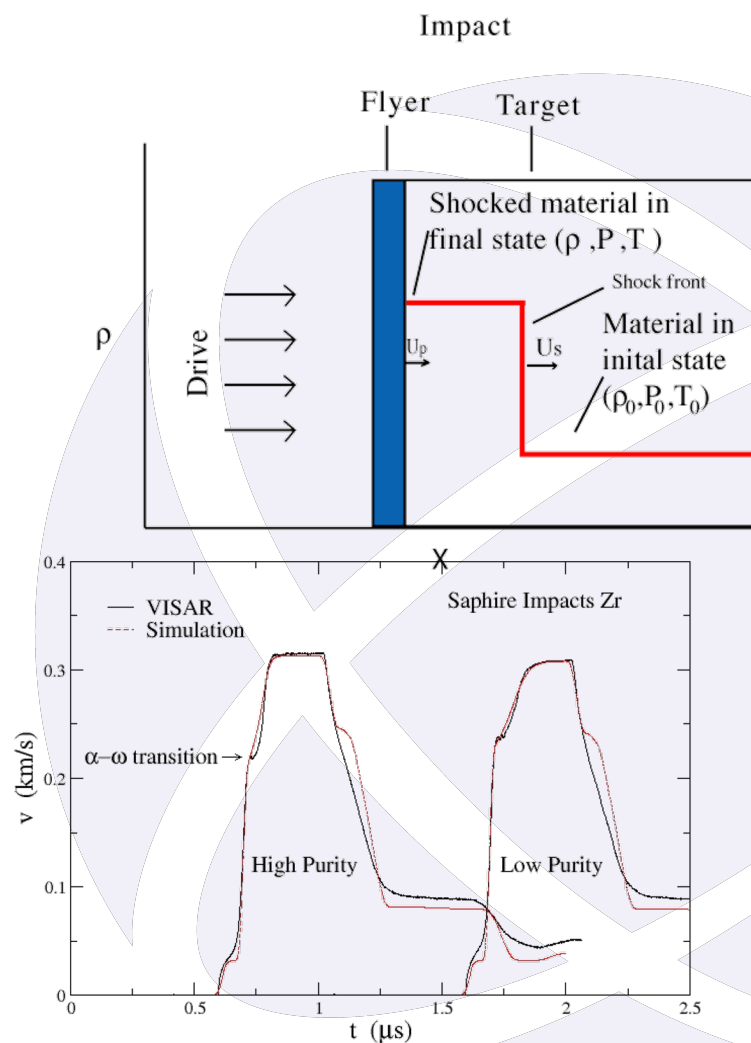
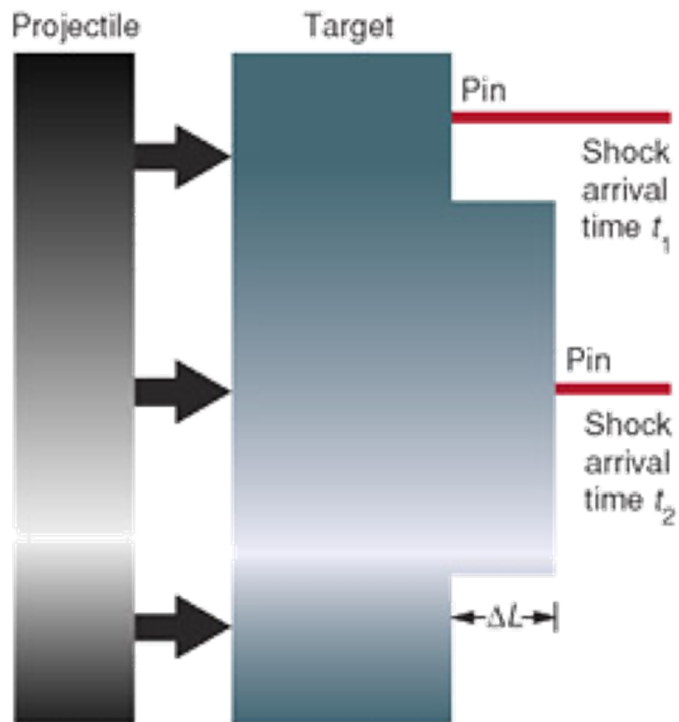
$$E_1 = E_0 + \frac{1}{2}(P_1 + P_0)(V_0 - V_1)$$

The “Hugoniot” (set of final states which can be achieved by a single shock) is typically represented in the  $(P,V)$ ,  $(u_s, u_p)$ , or  $(P, u_p)$  planes:

$$\frac{P_1 - P_0}{V_1 - V_0} = -(\rho_0 u_s)^2$$

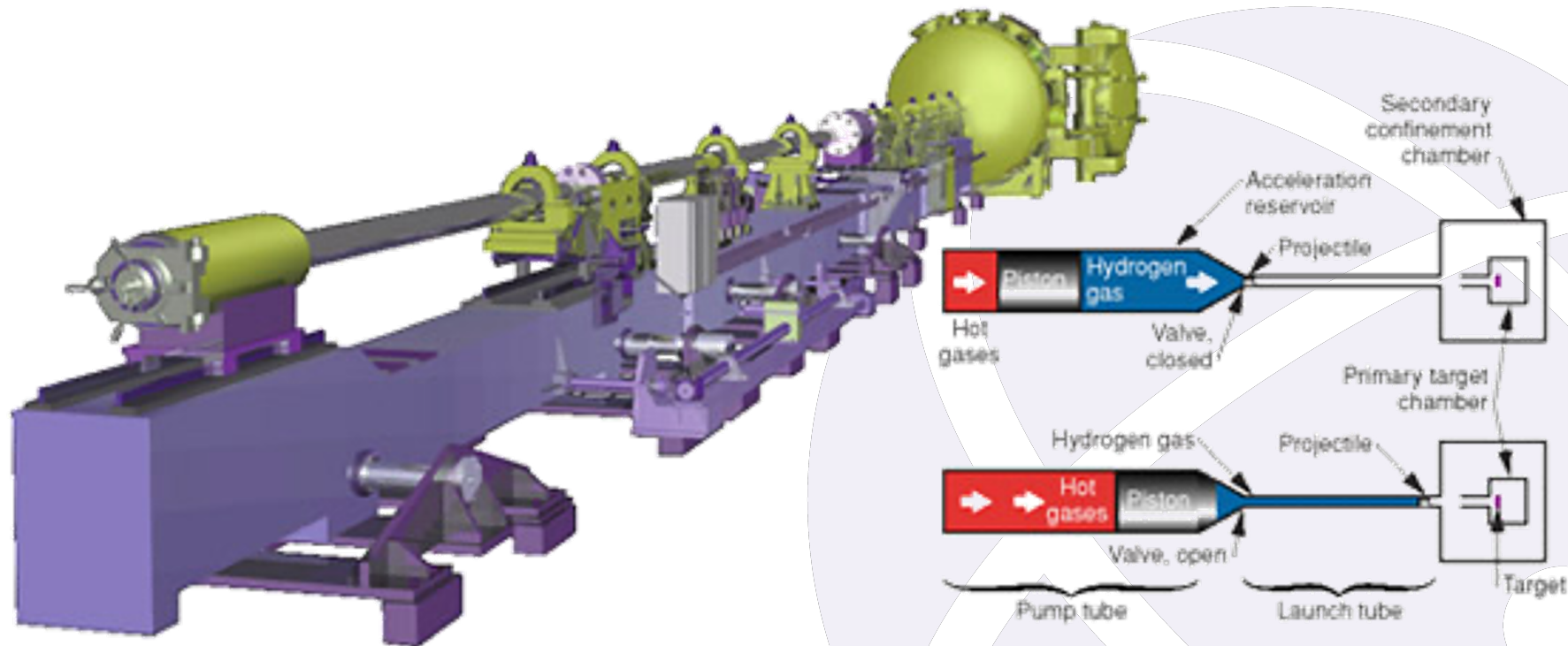


# Shock Physics



# Gas Gun

## Joint Actinide Shock Physics Experimental Research Two-stage light gas gun

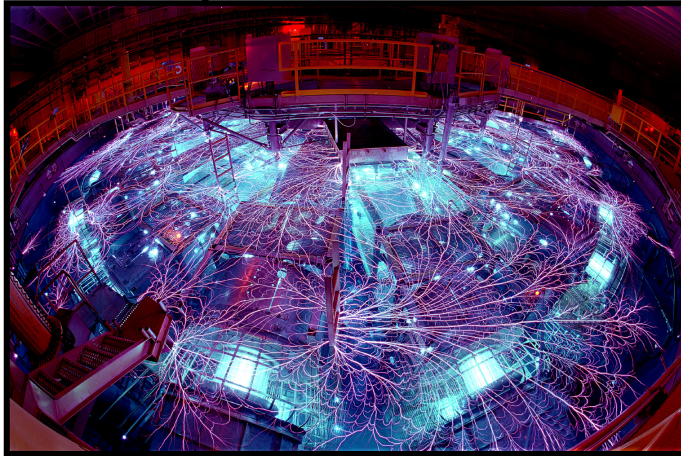
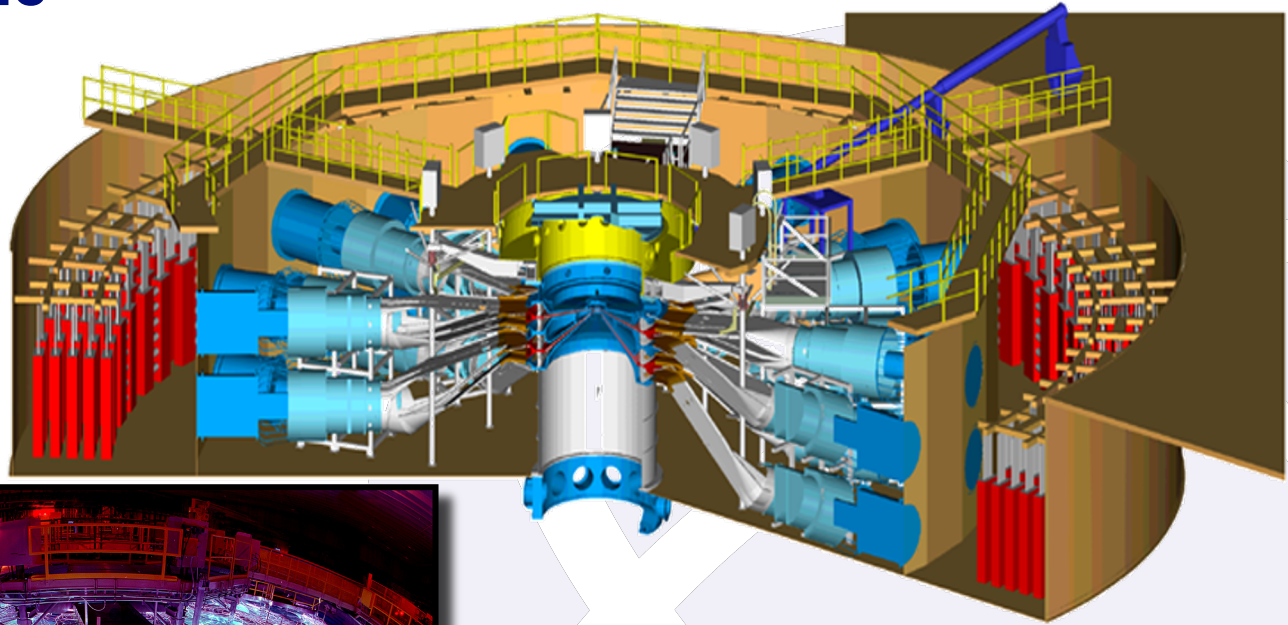


A schematic showing how a two-stage gas gun operates. In the first stage, hot gases from the powder propellant drive a piston, which compresses the Hydrogen gas in the pump tube. In the second stage, the high-pressure gas ruptures the valve, accelerating the projectile down the launch tube toward the target.

# Sandia's Z machine

11.5 MJ stored energy  
~22 MA peak current  
~200 ns rise time

~ 6 m



# Theoretical Methodologies for “Synthetic Data”

Why not just use experiment to produce data?:

These pressures are huge

P (Mbar)

0.000001	Ambient
1	Center of Earth
100	Center of Jupiter
340	Insulating Nickel
> 1340	Metallic Neon
350000	Center of Sun
1000000000	Highest $P_c$ for Al in SESAME

# Theoretical Methodologies for “Synthetic Data”

## Electronic Structure Methods

$$1 \text{ eV} = 11,604 \text{ K}$$

### Density Function Theory (DFT)

- Kohn-Sham (KS-DFT):  $T < 25 \text{ eV}$
- Orbital-Free (OF-DFT):  $T > 10 \text{ eV}$

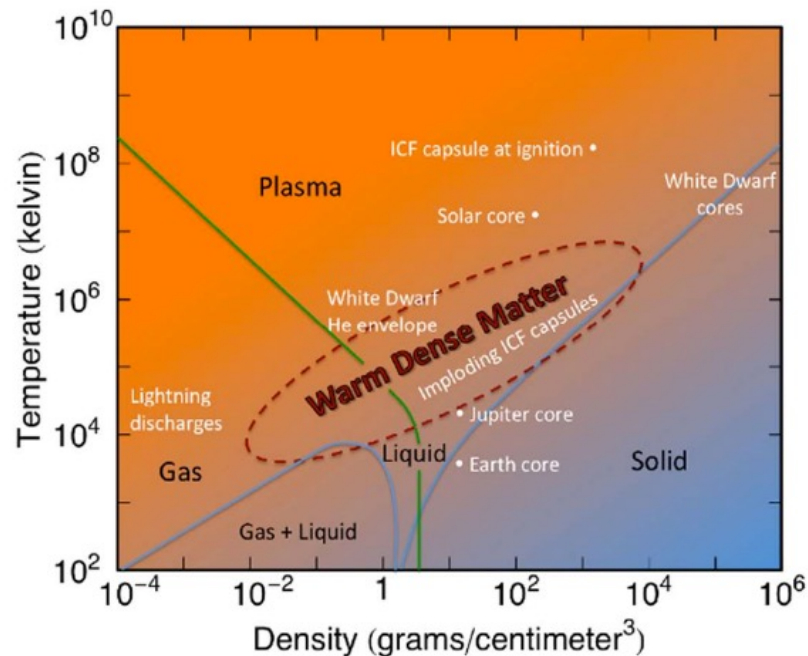
### Path Integral Monte Carlo

### Average atom models

### Plasma Models

## Molecular Dynamics (MD)

- Can be used with the above electronic structure theories



Travis Sjostrom: LA-UR 1623345

# Theoretical Methodologies for “Synthetic Data”

## Quantum Molecular Dynamics (QMD)

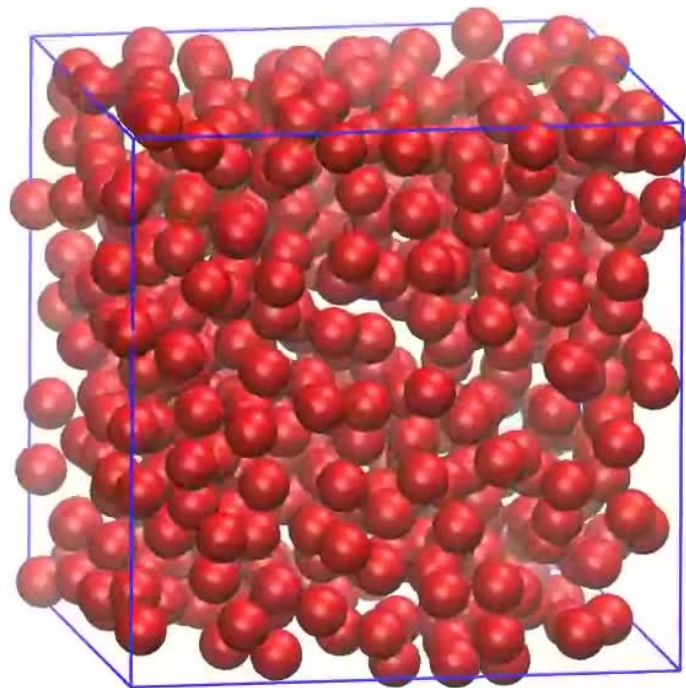
- Periodic Cell of N atoms
- Born-Oppenheimer approximation
- Electrons treated quantum mechanically

$$\left( -\frac{1}{2}\nabla^2 + U(\mathbf{r}, \mathbf{R}) \right) \Psi(\mathbf{r}, \mathbf{R}) = \epsilon_i \Psi(\mathbf{r}, \mathbf{R})$$

$$F_{elec}(\mathbf{R}) = -\frac{\partial U(\Psi(\mathbf{r}, \mathbf{R}))}{\partial \mathbf{R}}$$

- Ions treated classically  $\mathbf{F} = m\mathbf{a}$

$$m \frac{\partial^2 \mathbf{R}(t)}{\partial t^2} = F_{elec}(\mathbf{R}, t)$$



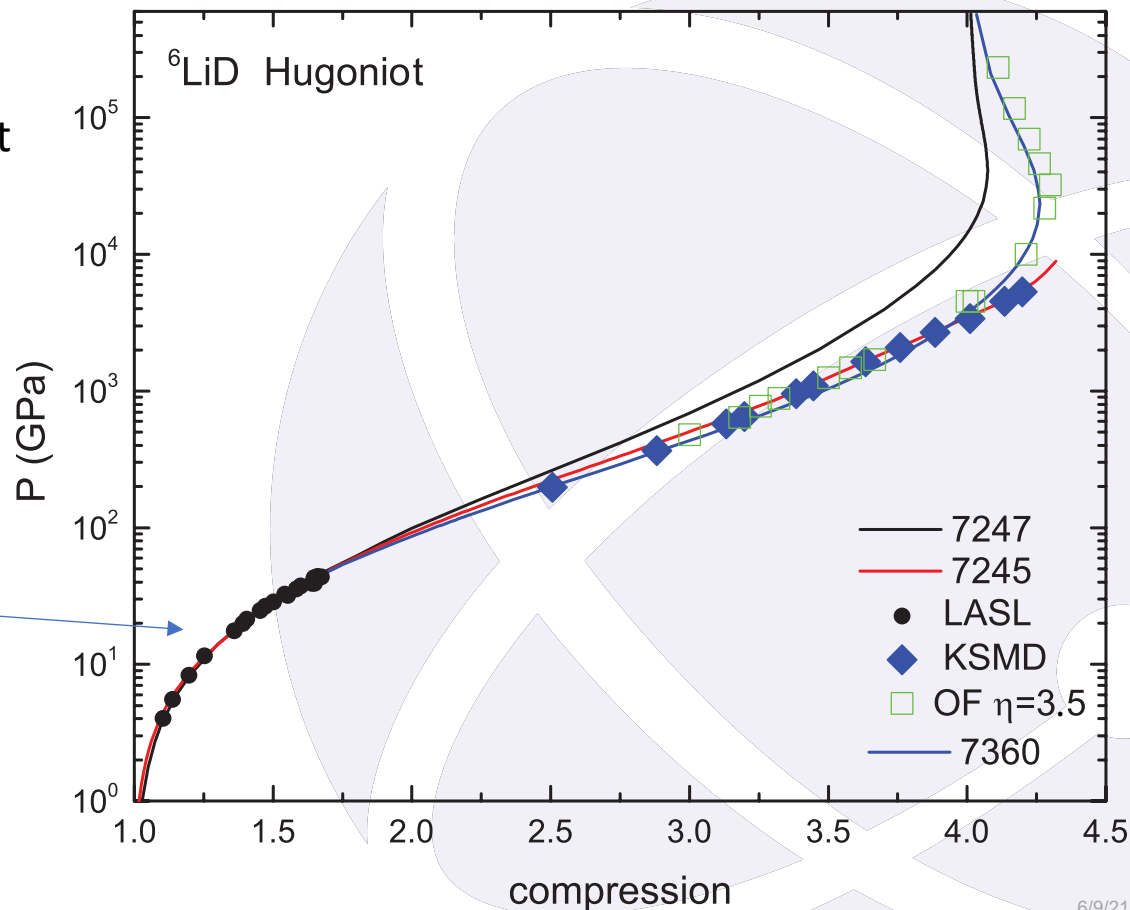
# Theoretical Methodologies for “Synthetic Data”

Using QMD to calculate Hugoniot

KSMD  $\sim T < 25\text{eV}$

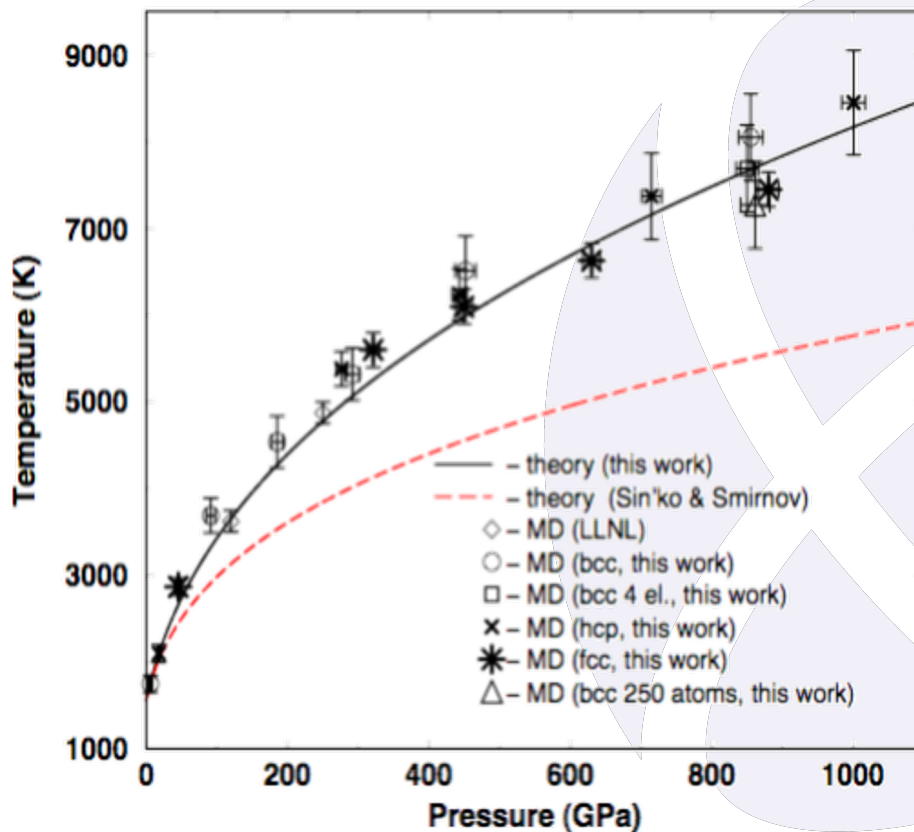
OFMD  $\sim T > 10\text{ eV}$

Experimental Shock data



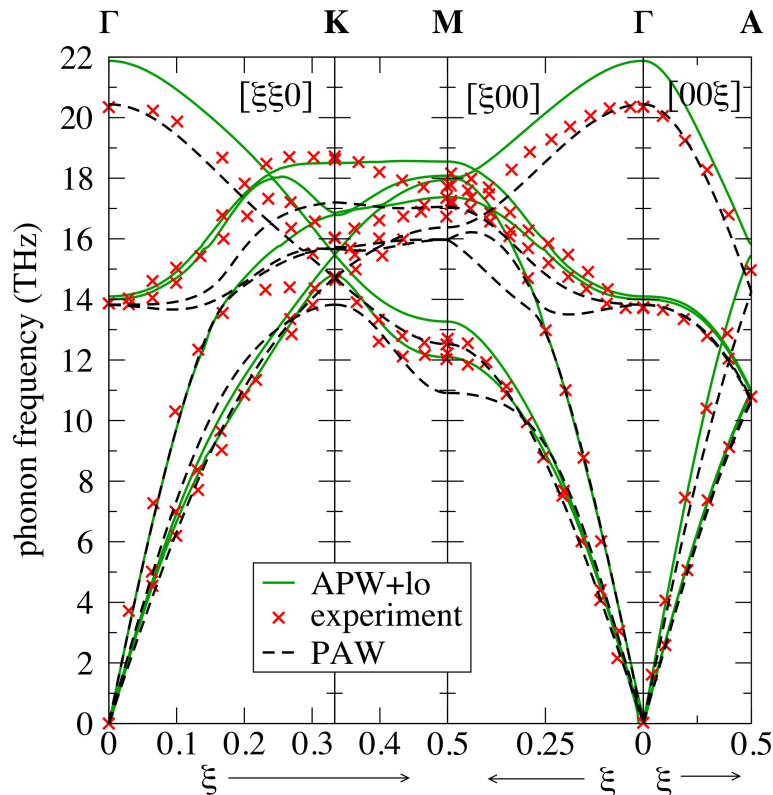
# Melt (Z-method) using QMD

Melt Curve for Be, credit Leonid Burakovsky

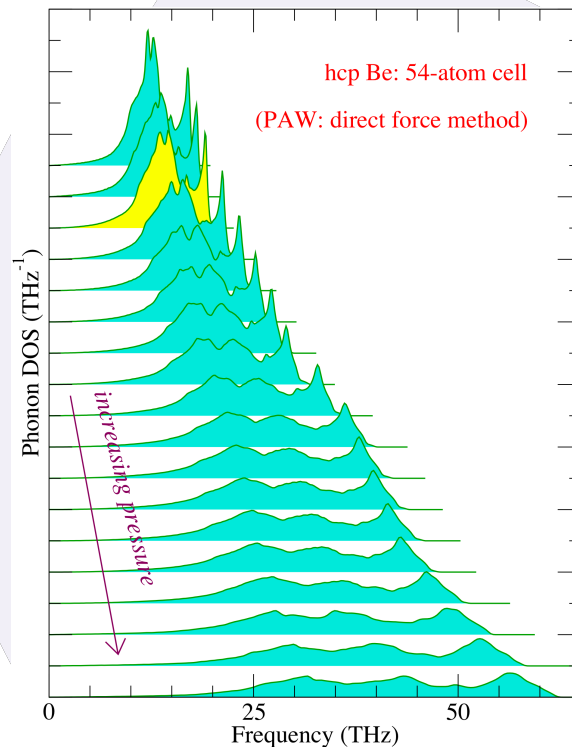


# Phonon dispersion and density of states via DFT

Provided by Sven Rudin, Be phonon calculations



Phonon density of state at a function of pressure



# LANL SESAME DATABASE: Tabular EOS

- Tabular vs. analytical
- Analytical EOS:
  - Typically well behaved and differentiable:  $PV = nRT$  (ideal gas)
  - Numerically stable
  - Limited to single phase or region of phase space where valid (low density, high T)
- Tabular:
  - Can be used over orders of magnitude ( $10^{-6} < \frac{\rho}{\rho_0} < 10^6$ ,  $0 < T < 10^9$ )
  - Can be fine tuned for solid, liquid, vapor, gas, and plasma regions
  - Relies on an interpolator (linear, spline, rational), Which is correct?
  - Some issues inverting independent variables (more later)

# Are all thermodynamic relations created equal?

Black: direct interpolation

Green: inverted with respect to second variable

Blue: constructed from two other tables

eospac6 calls

- EOS\_Pt\_DT, EOS\_Ut\_DT

- EOS\_Pt\_DUt

- EOS\_T\_DUt, EOS\_Pt\_DT

- EOS\_Pt\_DSt

- EOS\_St\_DPt

sound-speed derivation

$$c^2 = \left(\frac{\partial P}{\partial \rho}\right)_T + \frac{T}{\rho^2 \left(\frac{\partial U}{\partial T}\right)_\rho} \left(\frac{\partial P}{\partial T}\right)_\rho^2$$

$$c^2 = \left(\frac{\partial P}{\partial \rho}\right)_U + \frac{P}{\rho^2} \left(\frac{\partial P}{\partial U}\right)_\rho$$

$$c^2 = \left(\frac{\partial P}{\partial \rho}\right)_T + \left(\frac{\partial P}{\partial T}\right)_\rho \left[ \left(\frac{\partial T}{\partial \rho}\right)_U + \frac{P}{\rho^2} \left(\frac{\partial T}{\partial U}\right)_\rho \right]$$

$$c^2 = \left(\frac{\partial P}{\partial \rho}\right)_S$$

$$c^2 = \frac{-\left(\frac{\partial S}{\partial \rho}\right)_P}{\left(\frac{\partial S}{\partial P}\right)_\rho}$$

eq. label

(1) Menikoff

(2) FLAG

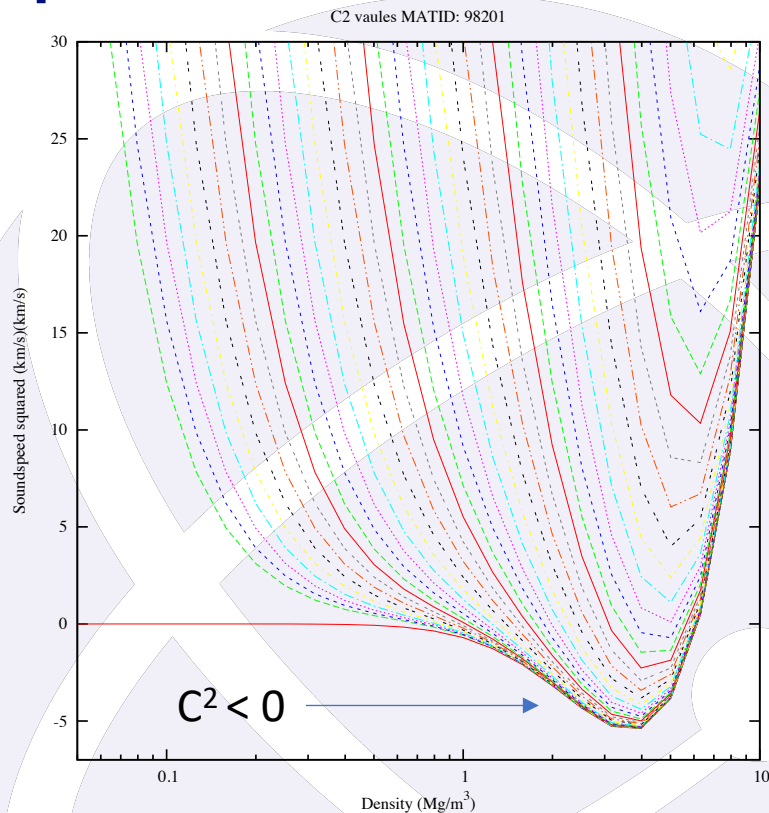
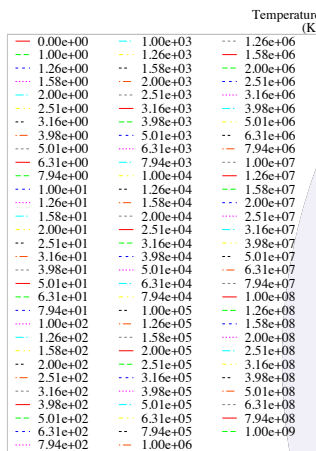
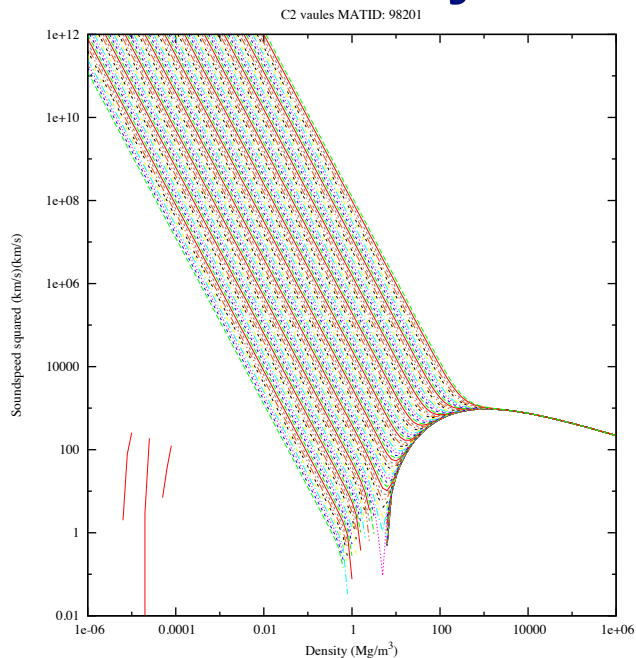
(3) Peterson

(4) entropy

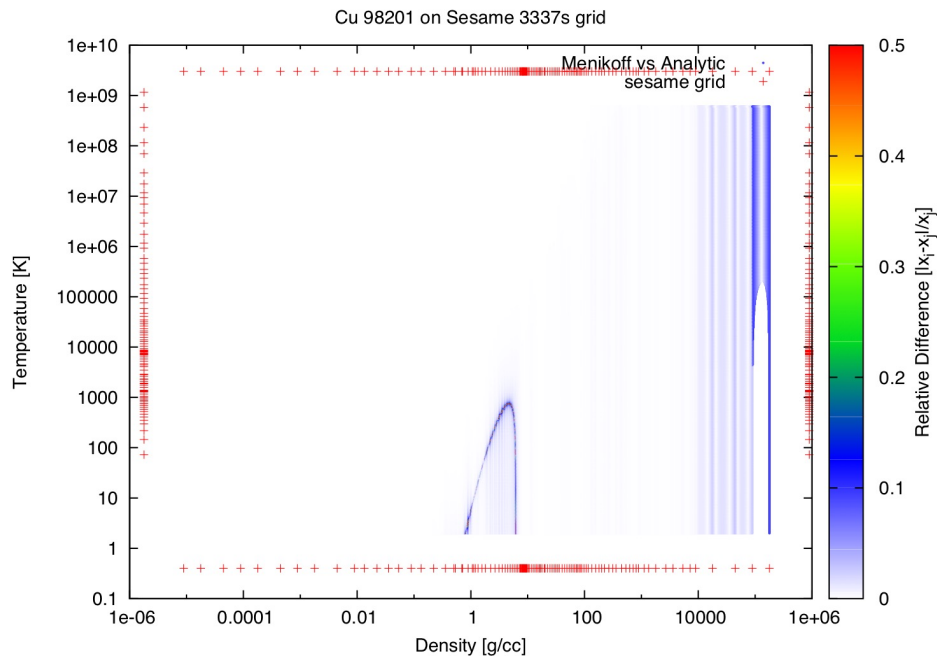
(5) entropy2

# What does the adiabatic sound speed look like for this analytic Cu eos?

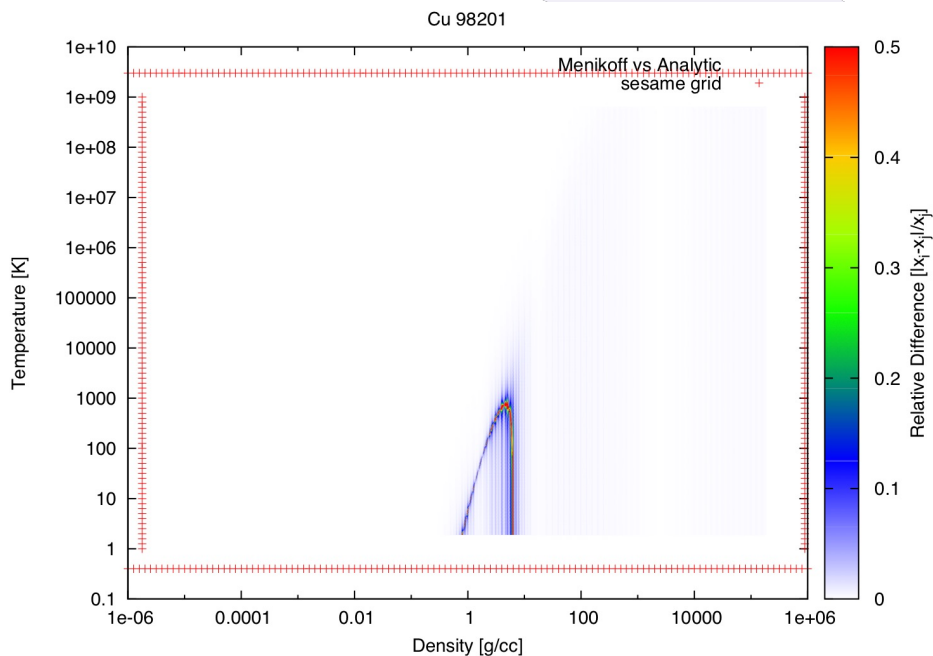
## C<sup>2</sup> vs Density



# Menikoff sound speed: Grid considerations

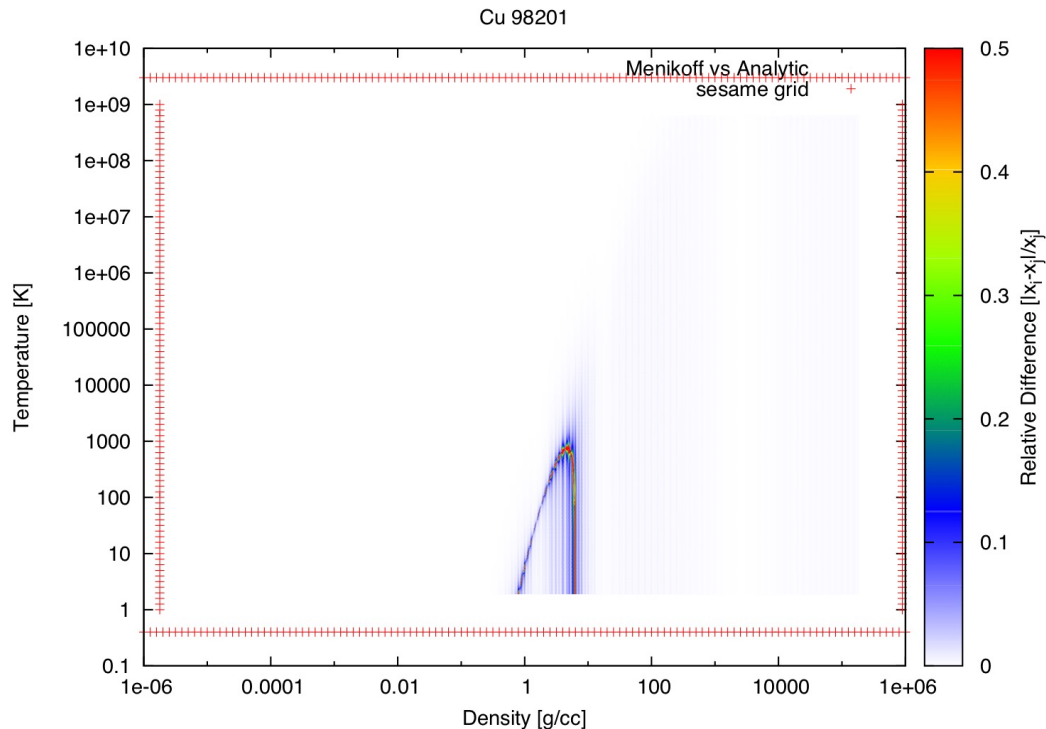


Typical Sesame Grid



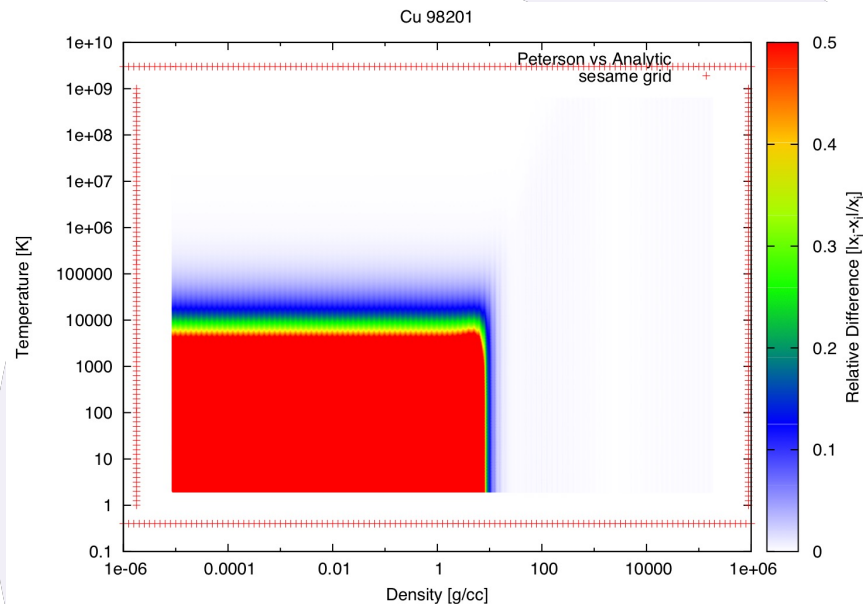
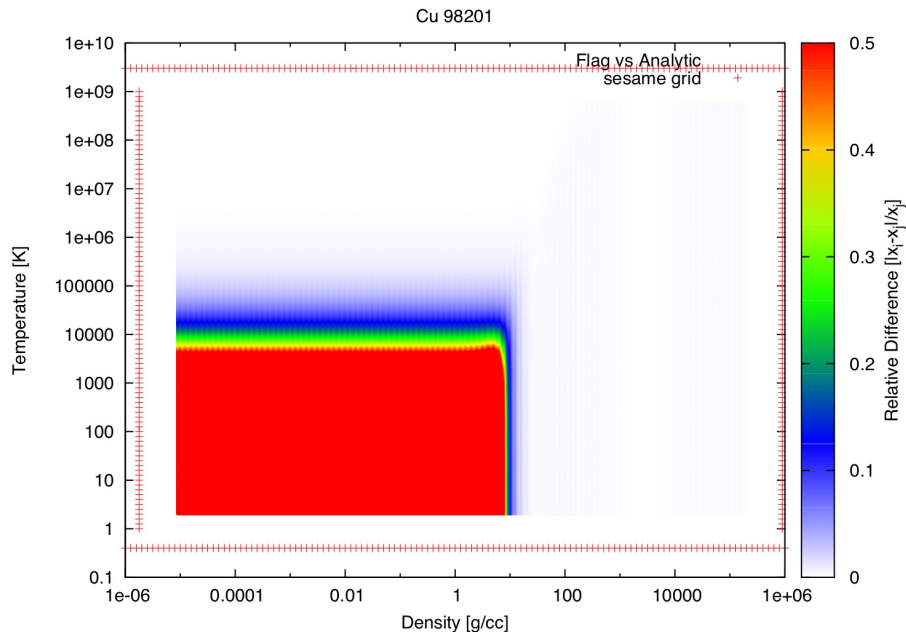
Even log spacing

# Menikoff does the best in expansion.



$$c^2 = \left( \frac{\partial P}{\partial \rho} \right)_T + \frac{T}{\rho^2 \left( \frac{\partial U}{\partial T} \right)_\rho} \left( \frac{\partial P}{\partial T} \right)_\rho^2$$

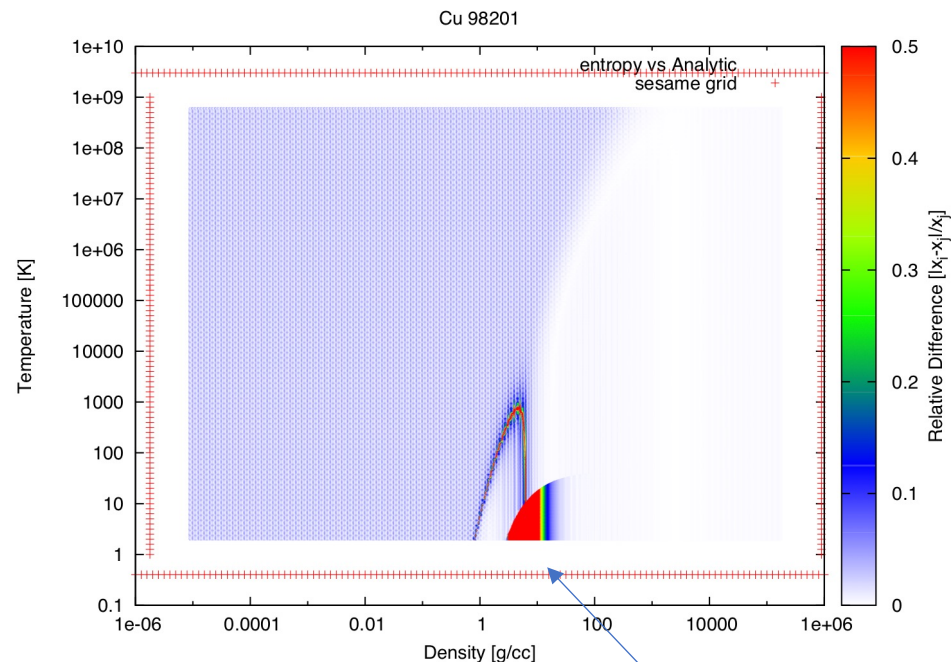
# Bad in expansion?



$$c^2 = \left( \frac{\partial P}{\partial \rho} \right)_U + \frac{P}{\rho^2} \left( \frac{\partial P}{\partial U} \right)_\rho$$

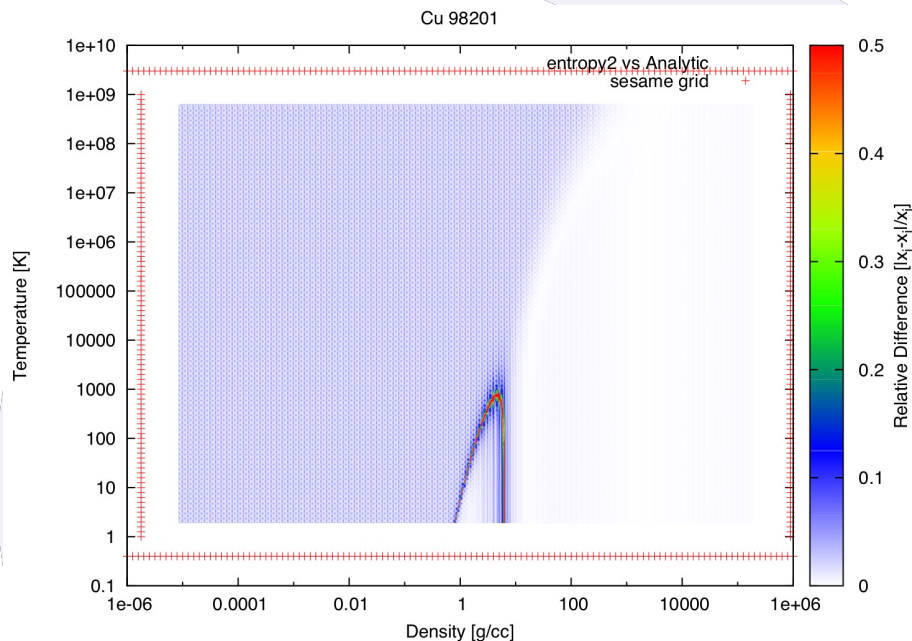
$$c^2 = \left( \frac{\partial P}{\partial \rho} \right)_T + \left( \frac{\partial P}{\partial T} \right)_\rho \left[ \left( \frac{\partial T}{\partial \rho} \right)_U + \frac{P}{\rho^2} \left( \frac{\partial T}{\partial U} \right)_\rho \right]$$

# Sound speed using a generated entropy table.



$$c^2 = \left( \frac{\partial P}{\partial \rho} \right)_S$$

Extrapolation



$$c^2 = \frac{-\left( \frac{\partial S}{\partial \rho} \right)_P}{\left( \frac{\partial S}{\partial P} \right)_\rho}$$